Spontaneous Emulsification of Pickering Emulsions without additives

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Chapter 1

Introduction

The making of permanent emulsions has been studied for many years, as it is important for foods, cosmetics, pharmaceutical preparations, and other products. The breaking of emulsions is also important in crude oil operations to recover the oil. Several types of emulsions have been researched for years, thus enhancing theoretical knowledge and industrial applications. The process and the conditions of emulsification are not completely known for all types of emulsions, due to the complexity and diversity of the systems. At the present time, there is no theory that seems to apply universally to all emulsions. That is probably because a number of factors contribute and the relative importance of each varies not only in different type emulsions but in the same type emulsion under different circumstances.

In this thesis, we investigate the formation conditions of surfactant free Pickering emulsions and the parameters that affect their stability. We focus on the equilibrium properties of Pickering emulsions, which are governed by electrostatics, entropic effects and adsorption. In this analysis, no dynamic effects are included, although the equilibrium results can possibly describe several mesostates of emulsion evolution towards phase separation. Including in the modeling of the Pickering emulsions the attributing interactions, we reach interesting results in accordance with recent experimental research [2].

In the following paragraphs, the characteristics of emulsions are discussed. In chapter 2, the main theoretical ideas required for the description of the investigated system are presented. In chapter 3, using the concepts of chapter 2, the theory of the spontaneous formation of Pickering emulsion is analyzed. In chapter 4, the numerical results obtained from the theory of emulsification are presented and discussed.

1.1 Colloids, Emulsions and Interfaces

A colloid or a colloidal dispersion is a mixture that consists of a continuous phase, called the dispersion medium, and a discontinuous phase, called the dispersed phase. The size of the objects of the dispersed phase is around $5nm - 10^3nm$, such that they can perform Brownian motion in the continuous phase. The objects can be solid particles or liquid droplets, although generally colloids can be made by any combination of gas, liquid, solid phase. A colloid of two or more immiscible liquids is called emulsion. A common example of two immiscible liquids is oil and water, which can form an emulsion given an energy input, in the form of shaking, beating or agitation. The provided energy is needed to separate the dispersed phase
into smaller globules, thereby increasing the surface area between the two liquids. In this way, more and smaller droplets of the dispersed medium into the continuous one can formed. The question is whether such a droplet state is stable.

The boundary surface between two different phases is called interface, in the case of emulsions an interface forms between two different liquids. The role of the interface is significant in the case that the area per volume is big, as in colloidal dispersions. After the formation of the emulsion, the droplets of the dispersed phase should be sufficiently small that they will stay suspended and that there should be a sufficiently viscous film in the interface to prevent coalescing. If the previous conditions are fulfilled, the emulsion may be stable over time. Nevertheless, stability is not trivial and in most of the cases emulsifying agents are used to increase stability.

The emulsifiers are usually surface active substances, that are adsorbed by the interface and form a coating that prevents coalescence of the droplets, for example substance such as egg, honey, mustard. A detergent is also an emulsifier, which reacts with both the oil and water phase, thus stabilizing the interface, as exemplified by the use of soap to remove fat. Sometimes the dispersed phase can act as its own emulsifier, that is the case of microemulsions, where the dispersed liquid forms nano droplets. A common example is the addition of water in a strong alcoholic anise-based beverage, like ouzo or raki, where a milky oil-in-water microemulsion is formed. Another type of stabilized emulsions are the so called Pickering emulsions, which are stabilized by solid particles, such as magnetite or silica, which are adsorbed by the oil-water interface. An example of Pickering emulsion is the homogenized milk, where proteins act as stabilizing particles.

### 1.2 Pickering Emulsions

Two interesting types of emulsions are microemulsions and Pickering emulsions. In both cases, the emulsions can be formed spontaneously, by the addition of the ingredients without energy input. The stabilization of microemulsion is achieved by surfactants and co-surfactants, whereas Pickering emulsions are stabilized by solid particles. Microemulsions consist of droplets of $5 - 100$ nm, whereas Pickering emulsions form droplets of $10 - 1000$ nm, therefore they are useful for different applications. A significant difference is that microemulsions reach thermodynamic equilibrium, whereas Pickering emulsions are in general only kinetically stable, thus the droplet state is metastable. In this thesis, we study two new types of Pickering emulsions, which both form spontaneously. The first exhibits kinetic stability in the absence of additives, and the second is thermodynamically stable with the addition of colloidal particles.

The recent experiments [2] on Pickering emulsions involved a specific type of oil and an aqueous solution of a specific type of salt, brought together to spontaneously form an emulsion. After a day the emulsion indeed formed, consisting of mono-disperse droplets [2, 3]. This emulsion without additives was found to be stable for a couple of days, after which the droplets start to coalesce leading to phase separation after a month [2]. If small colloidal particles are added, the formed emulsion is turned out to be stable for more than half a year. In addition, if such emulsions of different droplet sizes were mixed, an emulsion with an intermediate size of droplets was formed, suggesting thermodynamic stability [2, 3].

The theoretical model we develop, includes the essential phenomena that take place in
such a Pickering emulsion which we deem to be the electrostatic interaction among ions and charged oil droplets, adsorption effects in the oil-water interface and the ratio of interface area over volume. To model the emulsion, we consider a homogeneous system in equilibrium, which is composed of charged droplets of radius $a$ and ions of positive and negative charge. To treat the interactions between the ions and the charged spheres, as well as these among the droplets and the ions, each droplet is assumed to be isolated within a charge neutral cell of radius $R$. Each droplet has a charged surface, due to the adsorption of ions into the oil-water spherical interface. If small colloidal particles are added to the system, they are also adsorbed in the oil-water interface, that effect is not included in this thesis. The colloidal particles are neutral when added, but they can obtain charge by adsorption of positive and negative ions. The adsorption effect is described by the Langmuir isotherm. According to this mechanism, the surface of the adsorbent is uniform and consist of adsorption sites, where only one ion can bind. The adsorption of small colloidal particles in the oil-water interface decreases the surface area and favors the formation of droplets of the size of some decades nanometers.

In the next chapters, the theory we developed to describe the system is presented, as well as the results. We hope the result of this effort may contribute to an understating of such complex systems.
Chapter 2

Theoretical Background

In this section, several theories are mentioned in order to describe the system of interest in this work. In some cases, a meticulous description is presented, as it is useful for the following calculations. Other times several notions of classical mechanics, statistical physics and electrodynamics are used without further definition.

2.1 Classical Description of the System

The dynamical state of a classical system of \( N \) identical particles is described by a point in the \( 6N \) dimensional phase space \( \Gamma \), of positions and conjugate momenta. The evolution of the system in the phase space is driven by the Hamiltonian \( H \) of the system according to Liouville’s theorem. A short description of Liouville’s theorem using Poisson brackets is the following

\[
\frac{\partial p_s}{\partial t} = -\{p_s, H\},
\]

where \( p_s(r, p) \) represents the probability density of a microscopic state \( \Gamma = (r, p) \) of the system, where \( r = (r_1, r_2, ..., r_N) \) and \( p = (p_1, p_2, ..., p_N) \) are the position and momentum configuration.

The equilibrium state of the system does not depend on time, thus from Liouville’s theorem, \( \{p_s, H\} = 0 \). Therefore, the probability density of a microscopic state is a constant of motion and may be expressed as a function of other conserved quantities, such as the energy. In the next section, the microscopic statistical description is based on the distribution function as a function of the constant of the system such as energy and chemical potential.

2.2 Statistical Description of the System

The system is composed by a large number of particles, of the order of the Avogadro number \( (\approx 10^{24}) \), so it can also be treated as a statistical ensemble. Among the usual statistical ensembles, the most interesting ones to describe physical systems at a given temperature are the canonical and the grand canonical ensemble.

Thermodynamically, the microcanonical ensemble has constant volume \( V \), number of particles \( N \) and total energy \( E \). The canonical ensemble does not have constant total energy, but it exchanges energy with a heat bath that fixes the temperature \( T \). The grand canonical
ensemble in addition can also exchange particles with a reservoir of particles, that fixes the chemical potential $\mu$.

Considering the phase space of the system and the distribution function, the three ensembles can be described as follows. The distribution function of the microcanonical ensemble is non zero at the $(6N - 1)$ dimensional surface where the total Hamiltonian equals the total energy of the system. At the canonical ensemble, there is a set of such surfaces with energies $E \pm \Delta E$, where $E$ is the energy of the heat bath and $\Delta E$ the small fluctuations of the system. In the case of the grand canonical ensemble, the number of particles changes, so we can imagine the same set of surfaces as for the canonical case but the dimension of the surfaces fluctuates $(6(N \pm \Delta N) - 1)$.

By the normalization of the distribution functions, the partition functions arise. The partition functions indicate the way that the probabilities are partitioned among the different microstates that result to the same system energy. The importance of partition functions is the connection between the microscopic and macroscopic theory through the estimation of ensemble average of quantities such as the energy, the number of particles and the entropy. Following, we define the partition functions for the canonical and the grand canonical ensemble and connect them to macroscopic quantities.

### 2.2.1 Canonical Ensemble

The canonical partition function for a system of $N$ identical point particles, in a volume $V$ at temperature $T$ is defined as

$$ Z(N,V,T) = \frac{1}{N!h^{3N}} \int d^3r \int d^3p \, e^{-\beta H(r,p)}, \quad (2.2) $$

where $p = (p_1, p_2, ..., p_N)$ and $r = (r_1, r_2, ..., r_N)$ are the momentum and position configuration, respectively and $h$ is Planck constant. The canonical probability that the system is at a microstate of energy $H$ is given by

$$ p_c = \frac{1}{N!h^{3N}} \frac{e^{-\beta H}}{Z}. \quad (2.3) $$

Therefore, the average energy is given by

$$ \langle E \rangle = \int d^3r \int d^3p \, p_c H = \frac{1}{N!h^{3N}Z} \int d^3r \int d^3p \, e^{-\beta H} H $$

$$ = -\frac{1}{N!h^{3N}Z} \frac{\partial}{\partial \beta} \int d^3r \int d^3p \, e^{-\beta H} = -\frac{\partial \ln Z}{\partial \beta}. \quad (2.4) $$

The entropy is also derived as a function of the partition function

$$ S = -k_B \int d^3r \int d^3p \, p_c \ln p_c = \frac{-k_B}{N!h^{3N}Z} \int d^3r \int d^3p \, e^{-\beta H} \ln \frac{e^{-\beta H}}{Z} $$

$$ = -\frac{\partial \ln Z}{\partial \beta} + k_B \ln Z = k_B (\log Z + \beta \langle E \rangle). \quad (2.5) $$

The Helmholtz free energy $F$ is a thermodynamic potential depending on $(V, N, T)$, which in case of canonical ensemble are constant. It is also defined from the above relation by

$$ F = \langle E \rangle - TS = -k_B T \ln Z. \quad (2.6) $$
More thermodynamic quantities can be calculated from the free energy such as the pressure and the chemical potential

\[ p = -\left( \frac{\partial F}{\partial V} \right)_{N,T}, \quad \mu = \left( \frac{\partial F}{\partial N} \right)_{V,T}. \]  

(2.7)

### 2.2.2 Grand Canonical Ensemble

The grand partition function for a system of chemical potential \( \mu \), volume \( V \) and at temperature \( T \) is given as a weighted sum of partition functions with different number of particles

\[ \Xi(\mu, V, T) = \sum_{N=0}^{\infty} e^{\beta \mu N} Z(N, V, T). \]  

(2.8)

The grand canonical probability that the system of \( N \) particles is at a microstate \((r, p)\) of energy \( H(r, p) \) is

\[ p_{gc} = \frac{1}{N! h^{3N}} \frac{e^{-\beta H + \beta \mu N}}{\Xi}. \]  

(2.9)

The average number of particles is

\[
\langle N \rangle = \sum_{N=0}^{\infty} N \int d^3 r \ d^3 p \ p_{gc} \nonumber \\
= \sum_{N=0}^{\infty} N \frac{e^{\beta \mu N}}{N! h^{3N} \Xi} \int d^3 r \ d^3 p \ e^{-\beta H} \nonumber \\
= \sum_{N=0}^{\infty} N \frac{e^{\beta \mu N} Z(\mu, V, T)}{\Xi} = \frac{1}{\Xi} \frac{\partial}{\partial \beta \mu} \left( \sum_{N=0}^{\infty} e^{\beta \mu N} Z(\mu, V, T) \right) \nonumber \\
= \frac{\partial}{\partial \beta \mu} \ln \Xi. \]  

(2.10)

The grand potential \( \Omega \) is a thermodynamic potential depending on \((\mu, N, T)\), which in case of the grand canonical ensemble are constant. It is also defined as

\[ \Omega = \langle E \rangle - TS - \mu N = F - \mu N = -k_B T \ln \Xi. \]  

(2.11)

### 2.2.3 The Ideal Gas

The ideal gas is composed by randomly moving point particle that do not interact with each other. Even though it is a theoretical concept, it describes satisfactory dilute systems or it can be used as first approximation. The free energy and the chemical potential of the ideal gas is often used in the next chapter, so here we will derive those results.

The canonical partition function for \( N \) classical particles in volume \( V \) at temperature \( T \) with the interaction potential \( \Phi = 0 \) is given by Eq. (2.2)

\[ Z = \frac{1}{N! h^{3N}} \prod_{i=1}^{N} \int d^3 p_i \ e^{-\beta p_i^2 / 2m} = \frac{V^N}{N! \Lambda^{3N}}. \]  

(2.12)
where \( m \) is the mass of a particle and \( \Lambda \) is the thermal de Broglie wavelength \( \Lambda = \frac{h}{\sqrt{2\pi mk_B T}} \). The free energy is
\[
\beta F = -\ln Z = N \left( \ln \left( \frac{N \Lambda^3}{V} \right) - 1 \right),
\]
where the Stirling approximation \( \ln N! = N \ln N - N \) was used. The chemical potential is
\[
\beta \mu = \ln \rho \Lambda^3,
\]
where \( \rho = N/V \) is the particles density.

### 2.2.4 Binary Mixture of Ideal Gases

The previous description can be generalized for a system with different species of particles. The partition function for a different species reads
\[
Z(\{N_a\}, V, T) = \prod_a \frac{1}{N_a! \Lambda_a^3 N_a} \int d^3r_a \ e^{-\beta \Phi(r_a)},
\]
where \( r_a = (r_1, r_2, ..., r_{N_a}) \). The grand partition function is
\[
\Xi(\{\mu_a\}, V, T) = \prod_a \sum_{N_a=0}^{\infty} e^{\beta \mu_a N_a} Z(\{N_a\}, V, T)
\]
\[
= \prod_a \sum_{N_a=0}^{\infty} \frac{e^{\beta \mu_a N_a}}{N_a! \Lambda_a^3 N_a} \int d^3r_a \ e^{-\beta \Phi(r_a)}.
\]

In the case that all species are treated as ideal gas, the configurational integral of on particle is just the volume. For a binary mixture of two species of ideal gases these results read
\[
Z(\{N_a\}, V, T) = \frac{V^{N_1}}{N_1! \Lambda_1^{3N_1}} \frac{V^{N_2}}{N_2! \Lambda_2^{3N_2}},
\]
\[
\Xi(\{\mu_a\}, V, T) = \sum_{N_1=0}^{\infty} \frac{1}{N_1!} \left( \frac{V e^{\beta \mu_1}}{\Lambda_1^3} \right)^{N_1} \sum_{N_2=0}^{\infty} \frac{1}{N_2!} \left( \frac{V e^{\beta \mu_2}}{\Lambda_2^3} \right)^{N_2}
\]
\[
= e^{\frac{V e^{\beta \mu_1}}{\Lambda_1^3}} \exp \frac{V e^{\beta \mu_2}}{\Lambda_2^3} = e^{\frac{V \rho_1 \Lambda_1^3}{\Lambda_1^3}} \exp \frac{V \rho_2 \Lambda_2^3}{\Lambda_2^3}
\]
\[
= e^{\langle N_1 \rangle} e^{\langle N_2 \rangle}.
\]

### 2.3 Adsorption - Langmuir Isotherm

The adsorption of ionized molecules onto a surface is described by the Langmuir isotherm. To derive this, we assume an equilibrium among empty surface sites \( S \), ionized particles \( P^+ \) and sites filled with an ionized particle \( SP^+ \). The adsorption reaction is thus written as
\[
S + P^+ \rightarrow SP^+.
\]
The number of available sites is called $M$, while the number of occupied sites is $Z \leq M$. In addition, only one particle can bind to each site and the binding to one site is independent of the state (neutral or charged) of the other sites.

Under these circumstances, the partition function of the system with $Z$ particles being absorbed to $M$ surface sites is

$$ Z_p = \frac{M!}{Z!(M-Z)!} e^{-\beta F Z}, \quad (2.20) $$

where $F$ is the free energy of an occupied site. The more realistic case, that the number of occupied sites fluctuates, is described by the grand partition function, which from Eq. (2.8) is a linear combination of partition functions of different number of particles, such that

$$ \Xi = \sum_{Z=0}^{M} e^{\mu Z} Z_p = \sum_{Z=0}^{M} \left( \frac{M}{Z} \right)^e \beta^{(\mu-F)Z} = \left( 1 + e^{\beta(\mu-F)} \right)^M, \quad (2.21) $$

where $\mu$ is the chemical potential. The grand potential $\Omega$ of the system of adsorbed particles is

$$ \beta \Omega = -\ln \Xi = -M \ln \left( 1 + e^{\beta(\mu-F)} \right). \quad (2.22) $$

Therefore, the average value of the number of adsorbed ionized molecules is

$$ \langle Z \rangle = -\frac{\partial \Omega}{\partial \mu} = \frac{M}{1 + e^{\beta(F-\mu)}}, \quad (2.23) $$

which is also called the Langmuir isotherm. For fixed number of sites $M$ and free energy $F$, the Langmuir isotherm predicts that $\langle Z \rangle$ increases from $\langle Z \rangle \approx 0$ as $\mu \ll F$, to $\langle Z \rangle \approx M$ for $\mu \gg F$.

The number of occupied sites can be associated with an experimentally measurable quantity, the equilibrium constant $K$ of the reaction (2.19)

$$ K = \frac{[S][P^+]}{[SP^+]} = \frac{M - \langle Z \rangle}{\langle Z \rangle} \rho_{surf}, \quad (2.24) $$

where $[P^+] = \rho_{surf}$ is the local density of ionized particles at the surface. Solving this equation with respect to $\langle Z \rangle$,

$$ \langle Z \rangle = \frac{M}{1 + \frac{K}{\rho_{surf}}}, \quad (2.25) $$

yields the Langmuir isotherm in terms of the density of ions $P^+$ near the surface $\rho_{surf}$, the number of available sites $M$ and the equilibrium constant $K$ of the reaction (2.19). Comparing the two expressions, Eq. (2.23) with Eq. (2.25), we find a relation between the free energy and the equilibrium constant

$$ \frac{K}{\rho_{surf}} = e^{\beta(F-\mu)} \iff K = e^{\beta F} \Lambda^3, \quad (2.26) $$

where the chemical potential of the ideal gas $\beta \mu = \ln \rho \Lambda^3$ (2.14) is used. The free energy is given by the partition function $Z_p$ of a single particle in the external potential

$$ e^{-\beta F} = Z_p = \frac{1}{\Lambda^3} \int d^3 \mathbf{r} \ e^{-(\phi(\mathbf{r})+\phi_{surf})} \iff e^{-\beta F_0} = \frac{1}{\Lambda^3} \int d^3 \mathbf{r} \ e^{-\phi(\mathbf{r})}, \quad (2.27) $$
where $\phi(r)$ is the dimensionless interaction potential between an ion and a site and $\phi_{surf}$ the surface potential. In addition, the binding energy is defined by $F_b = F - \phi_{surf}$ and considered to be in the order of $1 - 10 \, k_BT$. Therefore, at room temperature the equilibrium constant is $K > 10^{-4}M$.

### 2.3.1 Another Langmuir Isotherm

Another type of Langmuir isotherm is derived for the following equilibrium among empty surface sites $S$, ionized particles $P^-$, filled ionized particle sites $SP^-$ and neutral molecules $A$

$$S + P^- \leftrightarrow SP^- + A. \quad (2.28)$$

We consider a two-state surface model of $Z_1$ ions that bind to available sites $S$, releasing $Z_1$ neutral molecules are released. A background concentration $\rho_m$ of molecules $A$ is added to the system, such that the total number of neutral $A$ type molecules is $Z_2 = Z_1 + \rho_m V$, where $V$ is the volume available to the $A$ molecules.

The partition function of this system, for $M$ surface sites and volume $V$ is given by

$$Z_p = \frac{M!}{Z_1!(M - Z_1)!} e^{-F_1 Z_1} \frac{V Z_2}{Z_2! \Lambda_2^3 Z_2}, \quad (2.29)$$

where $F_1 = F + F_f$ with $F$ the free energy of an occupied site and $F_f$ the free energy of the formation of a particle $A$. The thermal length of the neutral molecules is indicated by $\Lambda_2$.

The grand partition function of the system reads

$$\Xi = \sum_{Z_1=0}^{M} \sum_{Z_2=0}^{\infty} e^{\beta(\mu_1 + \mu_2)Z_1} Z_p$$

$$= \sum_{Z_1=0}^{M} \left( \frac{M}{Z_1} \right) e^{\beta(\mu_r - F_1)Z_1} \frac{V Z_2}{Z_2! \Lambda_2^3 Z_2} \quad (2.30)$$

$$= \left( 1 + e^{\beta(\mu_r - F)} \right)^M \frac{V Z_2}{Z_2! \Lambda_2^3 Z_2}, \quad (2.31)$$

where $\mu_1$, $\mu_2$ and $\mu_r = \mu_1 + \mu_2$ are the chemical potential of $SP^-$, $A$ and their sum respectively. Using the stirling approximation, the grand potential of the system is

$$\beta \Omega = - \ln \Xi = -M \ln \left( 1 + e^{\beta(\mu_r - F_1)} \right) + Z_2 \ln \frac{Z_2 \Lambda_2^3}{V} - Z_2. \quad (2.32)$$

Therefore, the average value of the number of absorbed ion and produced neutral molecules is

$$\langle Z_1 \rangle = - \frac{\partial \Omega}{\partial \mu_r} = \frac{M}{1 + e^{\beta(F_1 - \mu_r)}}, \quad (2.33)$$

where the partial derivative is with respect to the total chemical potential which characterizes the reaction at the equilibrium, as

$$\mu_S + \mu_{P^-} = \mu_{SP^-} + \mu_A = \mu_r. \quad (2.34)$$
The dimensionless equilibrium constant of this reaction is

\[
K = \frac{[S][P^-]}{[SP^-][A]} = \frac{(M - \langle Z_1 \rangle)\rho_{surf}}{(\langle Z_1 \rangle)(\rho_m V + \langle Z_1 \rangle)/V},
\]

which leads to equation

\[
\langle Z_1 \rangle = \frac{1}{2} \left(-1 + \sqrt{1 + x_i}\right) V(\rho_o + \rho_m)
\]

where \( x_i = \frac{4M\rho_o}{V(\rho_o + \rho_m)^2} \) and \( \rho_o = \frac{\rho_{surf}}{K} \).

This Langmuir not only depends on the density of ions near the surface \( \rho_{surf} \), the number of sites \( M \) and the equilibrium constant \( K \), but also on the background concentration \( \rho_m \) of \( A \) molecules and the volume \( V \).

Comparing the two Langmuir expressions, Eq. (2.23) and (2.36), a relation for the free energy and the reaction chemical potential \( \mu_r \) is found as

\[
e^{\beta(F_1 - \mu_r)} = \frac{1}{2} \left(1 + \sqrt{1 + x_i}\right) V(\rho_o + \rho_m) - 1,
\]

depending on the above parameters.

**Limit Cases of Langmuir Isotherm** Considering the expression (2.36) of the average number of absorbed ions, which depend on the parameter \( x_i \), two limiting cases arise for \( x_i \ll 1 \) and \( x_i \gg 1 \).

The first case, \( x_i \ll 1 \), occurs for large droplet radius or small number of sites \( M \). The square root is approximated by Taylor expansion and the following expression is obtained

\[
\langle Z_1 \rangle \approx M \left(1 + \frac{\rho_m}{\rho_o}\right) = \frac{M}{1 + \frac{K\rho_m}{\rho_{surf}}},
\]

which is very similar to the Langmuir isotherm (2.25) for a simple adsorption reaction. The relation suggests that the number of attached anions is tunable by the background concentration of \( A \).

The second case, \( x_i \gg 1 \), occurs for the opposite cases, small droplet radius or large oil volume fraction. The following expression is obtained

\[
\langle Z_1 \rangle \approx \sqrt{M\rho_o V}
\]

which, in contrast, is independent of the \( A \) concentration \( \rho_m \). The physics in this case depends only on the surface terms.

**2.3.2 Examples of Langmuir Isotherms**

Firstly, we assume the number of adsorbed ions given by Langmuir isotherm (2.25). We substitute the surface density by the Boltzmann distribution \( \rho_{surf} = \rho_s e^{-\phi(a)} \), where \( \rho_s \) is the bulk ion density and \( \phi(a) \) is the electrostatic potential at a sphere surface with radius \( a \).

Then we have from Eq. (2.25)

\[
\langle Z \rangle = \frac{M}{1 + \frac{K}{\rho_s} e^{-\phi(a)}},
\]
Figure 2.1: Langmuir isotherms of the type (2.25) and (2.36), as a function of the surface potential $\phi(a)$, for several parameter values.

This Langmuir isotherm is a Fermi-Dirac (FD) distribution, as also shown in Fig. (2.1(a)) (red thick line) as a function of $\phi(a)$, where the values of parameters $M$, $K$, $\rho_s$ are set to one. The rest three lines show the way the FD distribution changes by tuning the parameters. The purple, thick, and dashed dot line shows the change of the FD line by tuning the $K/\rho_s = 5$ ratio. The black, thick, and dashed line shows the change of the FD line by tuning the number of available sites to $M = 2$. The blue, thin, and dashed dot line shows the change of FD line by tuning both $K/\rho_s = 5$ and $M = 2$. The higher point depends on $M, Z \to M$ for $\phi(a) \to \infty$. The purple and blue line, with bigger $K/\rho_s$ ratio than one, decrease quicker.

Secondly, we assume the Langmuir isotherm (2.36) and apply the same substitutions as above at equation (2.41), therefore it reads

$$\langle Z_1 \rangle = \frac{1}{2} \left( -1 + \sqrt{1 + x_i} \right) V(\rho_o + \rho_m) \quad (2.42)$$

where $x_i = \frac{4M\rho_o}{V(\rho_o + \rho_m)^2}$ and $\rho_o = \frac{\rho_s e^{-\phi(a)}}{K} \quad (2.43)$

In Fig. (2.1(b)), the number of adsorbed ions is plotted as a function of the surface potential, with background density $\rho_m = 0$ and $\rho_m = 1$, for two different $\rho_s/K$ ratios. The dashed lines have $\rho_s/K = 0.4$ ratio, whereas the solid lines have $\rho_s/K = 1$ ratio. Adding background density $\rho_m = 1$, shifts both lines to the right.
2.4 Poisson-Boltzmann Equation

We consider a charged sphere of radius $a$ and point ions that screen the charged sphere. This can be described by the Poisson equation

$$\nabla^2 \phi(r) = -\frac{4\pi}{\epsilon} eQ(r),$$

(2.44)

where $\phi(r)$ is the electrostatic potential and $eQ(r)$, is the total charge distribution, such that

$$Q(r) = \rho(r) + q(r) = \rho_+(r) - \rho_-(r) + \sigma \delta(r - a),$$

(2.45)

where $\rho(r)$ is the average ion charge distribution and $q(r)$ is the external charge distribution, in this case the charged sphere. The average ion charge distribution is given by

$$\rho(r) = \rho_+(r) - \rho_-(r)$$

$$= \rho_s(g_+(r) - g_-(r))$$

$$= \rho_s(\exp(-\beta q\phi(r)) - \exp(\beta q\phi(r)))$$

$$= -2\rho_s \sinh(\beta q\phi(r)),$$

(2.46)

where $\rho_+$ and $\rho_-$ is the density distribution of positive and negative ions, $\rho_s$ is the bulk density of ions far from the sphere, $g_+$ and $g_-$ is the radial distribution function of positive and negative ions.

The radial distribution function $g_\pm(r)$ describes the way the cation (+) and anion (−) density vary as a function of the distance from a specific particle. For dilute liquids, the correlations are due to the potential energy, therefore using the Boltzmann law, $g(r)$ reads

$$g_\pm(r) = e^{\mp\beta\phi(r)}. \quad (2.47)$$

In the case of ideal gas particles, $g(r) = 1$ for all $r$. We also mention that $g(r \to \infty) = 1$, as $\phi(r \to \infty) = 0$.

Substituting the charge density to the Poisson equation, the Poisson-Boltzmann (PB) equation is obtained

$$\nabla^2 \phi(r) = \frac{8\pi e\rho_s}{\epsilon} \sinh(\beta e\phi(r)) - \frac{4\pi e\sigma}{\epsilon} \delta(r - a).$$

(2.48)

Using the dimensionless potential $\tilde{\phi}(r) = \beta e\phi(r)$, the PB equation takes the form

$$\nabla^2 \tilde{\phi}(r) = \kappa^2 \sinh(\tilde{\phi}(r)) - 4\pi \lambda_B \sigma \delta(r - a),$$

(2.49)

where $\lambda_B$ is the Bjerrum length and $\kappa^{-1}$ is the Debye length. The Bjerrum length is defined as the distance at which the electrostatic interaction between two unit charges equals $k_B T$,

$$\lambda_B = \frac{e^2}{\epsilon k_B T} \quad (2.50)$$

The Debye length denotes the typical distance at which the ionic charge screens out the surface charge of a hard sphere,

$$\kappa^{-1} = \sqrt{\frac{8\pi \lambda_B \rho_s}{\epsilon}} \quad (2.51)$$

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where $2\rho_s$ is the total ion density.

To solve the PB equation, appropriate boundary conditions should be imposed. The boundary conditions of a charged sphere of radius $a$ are

$$\frac{d\phi(r)}{dr}\bigg|_{r=\infty} = 0 \quad \text{and} \quad \frac{d\phi(r)}{dr}\bigg|_{r=a} = -4\pi\lambda_B\sigma,$$

(2.52)

where $\lambda_B$ is the Bjerrum length, $\sigma = Z/(4\pi a^2)$ the surface charge.

The PB equation, as a nonlinear equation, can be linearized and solved analytically. The linearized solution of PB equation gives satisfactory quantitively results for low charged surfaces. For higher charged surface, a numerical solution of the nonlinear PB equation is appropriate. In the following subsection, the dimensionless PB equation (A.1) is solved numerically. The dimensionless form of PB equation follows, with $x = r/a$, as

$$\frac{d^2\phi(x)}{dx^2} + \frac{2}{x} \frac{d\phi(x)}{dx} = \kappa^2 a^2 \sinh \phi(x),$$

(2.53)

where the dimensionless boundary conditions (2.52) are

$$\frac{d\phi(x)}{dx}\bigg|_{x=R/a} = 0 \quad \text{and} \quad \frac{d\phi(x)}{dx}\bigg|_{x=1} = -4\pi\lambda_B a\sigma = -\frac{\lambda_B}{a} Z.$$

(2.54)

(a) The electrostatic potential $\phi(r)$ surrounding a (b) The anion $\rho_-$, cation $\rho_+$ and total $\rho_+ - \rho_-$ charged colloid of radius $a = 100\lambda_B$ in a cell of radius $R = 2a$, in a medium of screening length $\kappa a = 3$. $a = 100\lambda_B$ in a cell of radius $R = 2a$, in a medium of screening length $\kappa a = 3$.

Figure 2.2: Electrostatic potential and densities plots, resulting by numerically solving the PB equation of a charged sphere of radius $a = 100\lambda_B$, surrounded by point ions in a cell of radius $R = 2a$, for screening parameter $\kappa a = 3$. 

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2.4.1 Numerical Solution of PB Equation

We consider a charged sphere of radius \( a \) in the center of a charged neutral cell of radius \( R \). Using the boundary conditions for a charged sphere (2.54)

\[
\frac{d\phi(x)}{dx} \Bigg|_{r=R} = 0 \quad \text{and} \quad \frac{d\phi(x)}{dx} \Bigg|_{x=1} = -\frac{\lambda_B}{a} Z
\]

(2.55)

and the dimensionless form of PB equation (2.53), the PB equation can be solved numerically on a radial grid

\[ x_i = a + i \frac{R - a}{N} \quad \text{with} \quad i = 0, ..., N , \]

(2.56)

between \( x = a \) and \( x = R \) with \( R \) the cell radius. The numerical method used to solve the PB equation is the Euler method, which can be found at appendix A.2.

Some illustrative results are presented in Fig. (2.2), using as cell radius \( R/a = 2 \), sphere radius \( a/\lambda_B = 100 \), charge \( Z = -1000 \) and screening length \( \kappa a = 3 \). The slope of the electrostatic potential at the cell boundary is zero, it indeed satisfies condition (2.55), indicating the charge neutrality of the cell. The positive and negative ionic densities tend to the bulk density at the boundary of the cell and the charge density tends to zero, supporting the charge neutrality of the cell. The ion densities follow from the Boltzmann distribution (2.47)

\[
\rho_{\pm}(r) = \rho_s e^{\mp \phi(r)}
\]

(2.57)

2.5 Density Functional Theory

The Density Functional Theory (DFT) is used to determine the structure of a many body system using functionals such as the spatially depended electron density. The two main principles of DFT are that

- the equilibrium properties of the system are uniquely determined by a particle density, therefore the many body system of \( 3N \) spatial coordinates is reduced to 3 spatial coordinates through the use of functionals
- defining and minimizing an energy functional for the system, a particle density arises, which is the equilibrium density of the system

A derivation of DFT can be found in sources [6, 7]. Using the notation of [6], we consider the grand potential functional \( \Omega \) of a system of \( N \) identical particles, interacting with a potential \( \Phi(r_1, r_2, ..., r_N) \), and an external potential \( V = \sum_{i=1}^{N} V_{ext}(r_i) \). We define the intrinsic local chemical potential as

\[
u(r) = \mu - V_{ext}(r),
\]

(2.58)

where \( \mu \) is the chemical potential. Using the functional derivative, the variation of the grand potential with respect to the intrinsic potential is

\[
\frac{\delta \Omega[u]}{\delta u(r)} = -\rho_0(r).
\]

(2.59)
where $\rho_0$ is the equilibrium density. The intrinsic Helmholtz free energy can be defined by the following Legendre transformation

$$ F[\rho_0] = \Omega[u] + \int \, d\mathbf{r} \, \rho_0(\mathbf{r}) u(\mathbf{r}) $$

Changing thermodynamic potential and independent function, the minimization condition (2.59) can be expressed as

$$ \frac{\delta F[\rho]}{\delta \rho(\mathbf{r})} = u(\mathbf{r}). $$

Hence, a system with a given external potential is associated with a unique equilibrium density and vice versa.

### 2.5.1 Examples of DFT

#### The Ideal Gas

The functional of the thermodynamic potential is calculated exactly for an ideal gas, like in equation (2.13) and also taking into account the spatially varying density. The functional of the intrinsic Helmholtz free energy of an ideal gas is

$$ \beta F_{id}[\rho] = \int \, d\mathbf{r} \, \rho(\mathbf{r}) (\ln \rho(\mathbf{r}) \Lambda^3 - 1), $$

by equation (2.60), using also equation (2.14) $\beta \mu = \ln \rho_s \Lambda^3$, the grand potential functional is

$$ \beta \Omega_{id}[\rho] = \int \, d\mathbf{r} \, \rho(\mathbf{r}) \left( \ln \frac{\rho(\mathbf{r})}{\rho_s} - 1 \right), $$

where $\rho_s$ is the bulk density of ideal particles.

#### Mean Field Approximation

About more interesting cases, where also interactions exist, the functional of the thermodynamic potential cannot be calculated exactly, hence approximation methods are applied. We are interested to Coulomb interaction, like a pairwise interaction can be approximated by the mean field approximation.

Using the perturbation theory, the interaction $v(\mathbf{r}, \mathbf{r}')$ is split into two parts, one without long range interactions $v_0(\mathbf{r}, \mathbf{r}')$ which is the reference system, and the other is a perturbation to the reference system, containing long range interactions $v_1(\mathbf{r}, \mathbf{r}')$. Hence, the interaction reads

$$ v(\mathbf{r}, \mathbf{r}') = v_0(\mathbf{r}, \mathbf{r}') + \lambda v_1(\mathbf{r}, \mathbf{r}'), $$

where $\lambda \in (0, 1)$ tunes the perturbation. As the reference system, the ideal gas can be used. The resulting free energy functional can be split into three parts

$$ \beta F[\rho] = F_{id}[\rho] + \frac{1}{2} \int_0^1 d\lambda \int \, d\mathbf{r} \int \, d\mathbf{r}' \rho_\lambda(\mathbf{r}) v_1(\mathbf{r}, \mathbf{r}') \rho_\lambda(\mathbf{r}') $$

$$ + \frac{1}{2} \int_0^1 d\lambda \int \, d\mathbf{r} \int \, d\mathbf{r}' h_\lambda^{(2)}(\mathbf{r}, \mathbf{r}') \rho_\lambda(\mathbf{r}) v_1(\mathbf{r}, \mathbf{r}') \rho_\lambda(\mathbf{r}'), $$

where $F_{id}$ is the free energy functional of the ideal gas and $h_\lambda^{(2)}(\mathbf{r}, \mathbf{r}')$ is the total correlation function. Within the mean field approximation the correlation term (third) is neglected and the density is substituted by the reference density $\rho_{id}(\mathbf{r})$. 19
Coulomb Interaction  We apply the mean field approximation to a system containing ion densities $\rho_\pm$ and an external field density $q(r)$, such that the charge density is $eq(r)$. As reference system, the ideal gas is considered. The long range interaction between the two kind of ions $\alpha_\pm$ is denoted by $v_{1\alpha,\alpha'}(r,r')$ and between the ions and the external field distribution is denoted by $v_{1\alpha,q}(r,r') = v_{1q,\alpha}(r,r')$ and both assumed to obey Coulomb law

$$v_{1\alpha,\alpha'}(r,r') = \frac{e^2}{\epsilon} \frac{\alpha \alpha'}{|r - r'|} \quad \text{and} \quad v_{1\alpha,q}(r,r') = \frac{e^2}{\epsilon} \frac{\alpha}{|r - r'|}. \quad (2.66)$$

Using the free energy functional (2.65) and Eq. (2.60), the grand potential functional is

$$\beta \Omega[\rho] = \beta \Omega_{id}[\rho] + \frac{1}{2} \sum_{\alpha,\alpha'=\pm} \int_V dr \int_V dr' \rho_\alpha(r) v_{1\alpha,\alpha'}(r, r') \rho_{\alpha'}(r')$$

$$+ \sum_{\alpha,\alpha'=\pm} \int_V dr \int_V dr' \rho_\alpha(r) v_{1\alpha,q}(r, r') q(r')$$

$$= \beta \Omega_{id}[\rho] + \frac{1}{2} \sum_{\alpha=\pm} \int_V dr \rho_\alpha(r) \left( \ln \frac{\rho_\alpha(r)}{\rho_s} - 1 \right) + \frac{1}{2} \int_V dr Q(r) \phi(r), \quad (2.67)$$

where $\rho_s$ is the bulk density of ions, the total charge density $Q(r) = \rho_+(r) - \rho_-(r) + q(r)$ and $\phi$ the dimensionless electrostatic potential

$$\phi(r) = \lambda_B \int_V \frac{dr'}{|r - r'|} \frac{Q(r')}{Q(r')}, \quad (2.68)$$

where $\lambda_B$ is the Bjerrum length, Eq. (2.50). Minimizing the grand potential functional (2.67) with respect to the ion densities $\rho_\pm$, results to Boltzmann distribution $\rho_\pm(r) = \rho_s \exp \pm \phi(r)$, which in combination with Poisson equation (2.44) leads to Poisson-Boltzmann equation (2.48)

$$\nabla^2 \phi(r) = \kappa^2 \sinh(\phi(r)) - 4\pi \lambda_B q(r) \quad (2.69)$$

Substituting the Boltzmann distributions to the functional (2.67), the equilibrium grand potential is found

$$\beta \Omega = 2 \rho_s \int_V dr \left( \frac{1}{2} \phi(r) \sinh \phi(r) - \cosh \phi(r) \right) + \frac{1}{2} \int_V dr q(r) \phi(r). \quad (2.70)$$
Chapter 3

Spontaneous Emulsification

3.1 Introduction

A Pickering emulsion is an emulsion that is stabilized by solid particles, such as magnetite, colloidal silica etc. The small colloidal particles are adsorbed onto the interface between the two phases, usually water and oil. This type of emulsion was named after its discoverer, S.U. Pickering [9]. An example of a Pickering emulsion is homogenized milk, where protein units are adsorbed at the surface of milk fat globules and act as a surfactant. Pickering emulsions usually are metastable, after a while they demix into macroscopic oil and water phases.

Some recent experimental findings suggesting that Pickering emulsion can be thermodynamically stable. This stimulated our interests to develop a theoretical model to describe the formation of this class of emulsions [4, 2]. We briefly mention the experimental results and then we introduce a theoretical model to describe thermodynamically stable Pickering emulsions.

The emulsions were synthesized by pouring together an oil called TPM (3 - (Methacryloxypropyl) tri-methoxysilane), an aqueous solution of TMAH salt (Tetramethylammonium hydroxide) and colloidal particles of the size of few nanometers, such as magnetite [4, 2]. After a day, an emulsion is formed spontaneously, consisting of water as the continuous phase and oil droplets as the dispersed phase. The oil droplets are covered by the colloidal nano particles, in this way the oil water interface reduces and the formation of finite droplet is favorable. The droplets are nearly mono-disperse in size. By mixing two systems of different droplet sizes a new system of intermediate droplet size arises, which suggests that the system is thermodynamically stable. The main difference with other Pickering emulsions is the spontaneous formation and the thermodynamical stability, which contrasts the kinetic stability that usually characterizes Pickering emulsions.

The following theory attempts to incorporate the key mechanisms of the formation and stability of emulsions. In section 3.2, we describe the spontaneous formation of emulsions without colloidal particles. However, this case is experimentally found to not be stable for a long time [2].
3.2 Theory of Spontaneous Emulsification

If oil and water are mixed and small oil droplets are formed and dispersed throughout the water, eventually the droplets will coalesce to decrease the amount of energy in the system. The energy of this the system is dominated by the interfacial term $\gamma_{ow}A_{tot}$, where $\gamma_{ow}$ is the oil-water surface tension and $A_{tot}$ the total surface area between oil and water. Denoting the number of droplets by $N_d$, such that $A_{tot} = N_d 4\pi a^2$ with $a$ the droplet radius, one easily checks that the surface energy per unit volume scales as

$$\frac{A_{tot}}{V_{tot}} = \frac{N_d A_d}{V_{tot}} = \frac{N_d A_d V_{oil}}{V_{tot} V_{oil}} = \frac{N_d A_d x}{N_d V_d} = \frac{3x}{a},$$

where $x = V_{oil}/V_{tot}$ is the oil volume fraction, with $V_{oil} = N_d V_d = N_d 4\pi a^3/3$. In Fig. 3.1, the interface contribution is plotted as a function of the droplet radius $a$ for different oil volume fractions. Regardless $x$, the favorable state is reached at $a \to \infty$ where the system is macroscopically phase separated.

![Figure 3.1: Area over volume term plotted versus the droplet radius $a$, for different oil volume fractions. The minimum occurs at $a \to \infty$ when the system phase separate. For small oil volume fractions $x$, the function drops to zero quicker than for larger $x$.](image)

However, if we assume that ions can be adsorbed onto the oil-water interface, they compensate the interface term and hence thermodynamically stable emulsions can be formed. By adding salt to the water, cations are produced from dissociation. The anions are produced by the hydrolysis and dissociation of the oil. Both can be adsorbed by the oil water interface. The pairwise Coulomb interaction between ions is also considered. The competition among area over volume fraction, electrostatics and adsorption effects results to stable droplets of finite size.
3.2.1 Chemical Reactions and Adsorption

During the mixing of the oil TPM (3-(Methacryloxypropyl) trimethoxysilane) with an aqueous solution of TMAH salt (Tetramethylammonium hydroxide) the following processes take place. The alkalic environment produced by the dissociation of the TMAH salt into TMA$^+$ and OH$^-$, enhances the hydrolysis of the TPM oil, which produces negatively charged TPM$^-$ molecules of hydrolyzed oil. Both TMA$^+$ cations and TPM$^-$ anionic molecules of hydrolyzed oil are amphiphilic and consequently surface active. Therefore, they have a tendency to adsorb onto the oil water interface and lower the interfacial tension.

A simple way to describe these complicated multi-step reactions is by the two following schematic reactions. The cations TMA$^+$ may be adsorbed at sites $S$ of the surface of the oil droplet, contributing to a positive surface charge. The net reaction is,

$$\text{TMA}^+ + S \leftrightarrow \text{STMA}^+ \quad (3.2)$$

The hydrolysis of the TPM oil and the dissociation of the hydrolyzed molecules can jointly be described by the following equivalent reaction

$$\text{TPM} + \text{OH}^- \leftrightarrow \text{CH}_3\text{OH} + \text{TPM}^- \quad (3.3)$$
where h at TPM$_h$ stands for hydralyzed. Note that methanol, CH$_3$OH, is formed which is presumed to be dissolved in the water phase.

3.2.2 Responsive Oil Model

We consider $N_d$ oil droplets of radius $a$ in a volume $V$, surrounded by an aqueous ionic solution. Each droplet is presumed in the center of a charge neutral cell of radius $R$, whose size depends on the fixed volume fraction $x$ of the droplets, $x = 4\pi a^3N/3V$, such that the radius is $R = ax^{-\frac{1}{3}}$. The droplets have a surface charge $e\sigma$ due to adsorption and reactions of oil and ions at the oil-water interface. Symmetry over the polar angle $\theta$ and the azimuthal angle $\phi$ is assumed, such that we deal with a radially symmetric geometry of a single droplet in a finite spherical cell.

The cations and anions can be absorbed at sites S on the surface of the droplet. The number of available sites per area is $M/4\pi a^2 = O(10)$ nm$^{-2}$ and they are accessible for anions and cations. The total grand potential per system volume is a physical quantity, which yields important information of the system. By minimizing this quantity with respect to droplet radius, the optimal size of droplets is obtained. If we assume that total grand potential is $\Omega_{tot} = N_d\Omega_{cell}$, where $N_d$ is the number of droplet and cells, we can write

$$\frac{\Omega_{tot}}{V_{tot}} = \frac{N_d\Omega_{cell}}{N_dV_{cell}} = \frac{\Omega_{cell}}{V_{cell}},$$

where $V_{cell} = 4\pi R^3/3$ is the volume of the cell. The dimensionless form we consider, is $\beta\Omega_{cell}/\rho_sV_{cell}$, where $\rho_s$ the bulk salt concentration in the water phase, we presume the oil to be salt free.

The total grand potential depends on the density profiles $\rho_{\pm}(r)$ and the total number of cations $Z_c$ and anions $Z_a$ adsorbed. They determined by the oil volume fraction $x$ and the droplet radius $a$ though the volume of the cell and the droplet respectively. The grand potential reads

$$\beta\Omega_{cell}(\rho, Z_c, Z_a) = 4\pi \sum_{a = \pm} \int_a^R dr \ r^2 \rho_a \left( \ln \frac{\rho_a}{\rho_s} - 1 \right) + \frac{1}{2} 4\pi \int_a^R dr \ r^2 \phi(r) Q(r)$$

$$+ 4\pi a^2 \beta\gamma_{ow} + \beta\Omega_1 + \beta\Omega_2,$$

where $Q(r) = \rho_+(r) - \rho_-(r) + \sigma\delta(r-a)$ with $\sigma = (Z_c - Z_a)/4\pi a^2$ the surface charge distribution, $\gamma_{ow}$ is the interfacial tension and $\phi(r)$ is the potential satisfying the Poisson-Boltzmann equation (2.49). From now on, we will use $\Omega$ to represent $\Omega_{cell}$. The grand potential term $\Omega_1$ is the additional contribution of the cation adsorption (3.2),

$$\beta\Omega_1 = Z_c(\beta F_c - \beta \mu) - \ln \left( \frac{M}{Z_c} \right),$$

where $\beta F_c = \ln K_c A^3$ is the cations binding energy with $K_c$ the equilibrium constant of reaction (3.2)

$$K_c = \frac{[\text{TMA}^+][S]}{[\text{STMA}^+]}.$$
and $\beta \mu = \ln \rho_s \Lambda^3$ is the cation chemical potential with $\Lambda$ the thermal de Broglie length. The grand potential term $\Omega_2$ is the additional contribution of the reaction (3.3) and the adsorption of anions at the oil water interface,

$$\beta \Omega_2 = Z_a (\beta F_a - \beta \mu) - \ln \left( \frac{M}{Z_a} \right) + Z_a \ln \left( \frac{Z_a \Lambda^3}{V_a} - 1 \right), \quad (3.8)$$

where $\beta F_a = \ln K_a$ is the anions binding energy with $K_a$ the equilibrium constant of reaction (3.3)

$$K_a = \frac{[\text{OH}^-][\text{TPM}]}{[\text{CH}_3\text{OH}][\text{TPM}^{-h}]} \quad \text{.} \quad (3.9)$$

The volume $V_a = 4\pi R^3(1 - x)/3$ is the available volume for the methanol and the third term of $\Omega_2$ is the free energy of the methanol, treated as an ideal gas.

If the grand potential is minimized with respect to ion densities $\rho_{\pm}$, we have

$$\frac{\delta \beta \Omega}{\delta \rho_{\pm}(r)} = \ln \frac{\rho_{\pm}(r)}{\rho_s} \pm \phi(r) = 0, \quad (3.10)$$

which leads to Boltzmann distributions for $\rho_{\pm}$,

$$\rho_{\pm}(r) = \rho_s e^{\mp \phi(r)}, \quad (3.11)$$

where the potential $\phi(r)$ is the solution of the PB equation (2.49) with boundary conditions $\phi'(a) = -4\pi \lambda_B \sigma$ and $\phi'(R) = 0$. Substituting the densities distributions to Eq. (3.5), gives

$$\beta \Omega(Z_c, Z_a) = \rho_s \int d^3r \left( \phi(r) \sinh \phi(r) - 2 \cosh \phi(r) \right) + 4\pi a^2 \beta \gamma_{ow}$$

$$+ \frac{1}{2} \int d^3r \phi(r) \sigma (r-a) + \beta \Omega_1 + \beta \Omega_2. \quad (3.12)$$

Minimizing the grand potential (3.12) with respect to cation charge number $Z_c$, leads to

$$\frac{\delta \beta \Omega}{\delta Z_c} = \ln \frac{Z_c}{M - Z_c} + \phi(a) + \beta F_c - \beta \mu = 0, \quad (3.13)$$

which can be rewritten into the Langmuir isotherm

$$Z_c = \frac{M}{1 + \frac{K_c}{\rho_s} e^{\phi(a)}}, \quad (3.14)$$

with $K_c$ defined in (3.7). Minimizing the grand potential with respect to anion charge number $Z_a$, leads to

$$\frac{\delta \beta \Omega}{\delta Z_a} = \ln \frac{Z_a}{M - Z_a} - \phi(a) + \beta F_a - \beta \mu + \ln \left( \frac{Z_a \Lambda^3}{V_a} \right) = 0, \quad (3.15)$$

which can be written as the following Langmuir isotherm,

$$Z_a = \frac{1}{2} \left( -1 + \sqrt{1 + \xi} \right) V_a \rho_o, \quad (3.16)$$

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where
\[ \xi = \frac{4M}{V_a \rho_o} \quad \text{and} \quad \rho_o = \frac{\rho_s e^{\phi(a)}}{K_a}. \]

Substituting the Langmuir isotherms and approximating the binomial coefficients by the Stirling approximation, the final form of the grand potential is
\[ \beta \Omega(Z_c, Z_a) = \rho_s \int d^3r \left( \phi(r) \sinh \phi(r) - 2 \cosh \phi(r) \right) \]
\[ + 4\pi a^2 \beta \gamma_{ow} - \frac{1}{2} \phi(a)(Z_c - Z_a) - Z_a \]
\[ + M \ln \left( 1 - \frac{Z_c}{M} \right) + M \ln \left( 1 - \frac{Z_a}{M} \right), \]
\[ (3.18) \]
where \( \phi(r) \), \( Z_c \) and \( Z_a \) are the solution of the PB equation and the Langmuir isotherms (3.14) and (3.16), respectively.

### The Macroscopic Limit

The limit of the total grand potential (3.18) per oil droplet, for the oil droplet radius \( a \to \infty \) going to infinity gives
\[ \lim_{a \to \infty} \frac{\beta \Omega}{\rho_s V_{cell}} = -2 \frac{V_{cell} - V_{drop}}{V_{cell}} = -2(1 - x), \]
\[ (3.19) \]
which stems from the first line of Eq. (3.18), since the remaining ones drop with \( 1/a \) behavior.

### 3.2.3 Methanol Buffering

In this section, the previous description of water-oil emulsions will be studied with the addition of a background methanol concentration. The extra methanol concentration changes the reaction rate and consequently the charge of the oil droplets. Therefore, the equilibrium state of the system changes. The background methanol concentration together with the oil volume fraction and the salt concentration are parameters that give the ability to tune the equilibrium radius of the droplet and the stability of the system.

To present this system, the same analysis as for the previous section is assumed. The parts mentioned are the modified ones by the extra methanol in the mixture.

The grand potential term \( \Omega_2 \) related to the anions adsorption and methanol release (3.3), including the background concentration of methanol now becomes
\[ \beta \Omega_2 = Z_a(\beta F_a - \beta \mu) - \ln \left( \frac{M}{Z_a} \right) \]
\[ + (\rho_m V_a + Z_a) \left( \ln \left( \rho_m V_a + Z_a \right) \Lambda^3 - 1 \right), \]
\[ (3.20) \]
where \( V_a = V_{cell}(1 - x) \) is the available volume for methanol.

Minimizing the grand potential with respect to anion charge number \( Z_a \), now leads to
\[ \frac{\delta \beta \Omega}{\delta Z_a} = \ln \frac{Z_a}{M - Z_a} - \phi(a) + \beta F_a - \beta \mu + \ln \left( \frac{\rho_m V_a + Z_a}{V_a} \right) \Lambda^3 = 0, \]
\[ (3.21) \]

26
which can be written as the Langmuir isotherm,

\[ Z_a = \frac{1}{2} \left( -1 + \sqrt{1 + \xi} \right) V_a (\rho_o + \rho_m), \]  

(3.22)

where

\[ \xi = \frac{4M\rho_o}{V_a (\rho_o + \rho_m)^2} \quad \text{and} \quad \rho_o = \frac{\rho_s e^{\phi(a)}}{K_a}. \]  

(3.23)

Substituting the Langmuir isotherms and approximating the binomial coefficients by the Stirling approximation, the final form of the grand potential is

\[
\beta \Omega(Z_c, Z_a) = \rho_s \int d^3 r \left( \phi(r) \sinh \phi(r) - 2 \cosh \phi(r) \right)
+ 4\pi a^2 \beta \gamma_{ow} - \frac{1}{2} \phi(a) (Z_c - Z_a) - \rho_m V_a - Z_a
+ M \ln \left( 1 - \frac{Z_c}{M} \right) + M \ln \left( 1 - \frac{Z_a}{M} \right).
\]  

(3.24)

The Macroscopic Limit

The limit of the modified total grand potential (3.24) per oil droplet, for the oil droplet radius \( a \rightarrow \infty \) going to infinity gives

\[
\lim_{a \rightarrow \infty} \frac{\beta \Omega}{\rho_s V_{cell}} = -2 \frac{V_{cell} - V_{drop}}{V_{cell}} - \frac{\rho_m}{\rho_s} (1 - x) = -(2 + \frac{\rho_m}{\rho_s})(1 - x).
\]  

(3.25)

The non zero terms are the first one and the term \(-\rho_m V_a\) of Eq. (3.24), the remaining ones drop with \(1/a\) behavior.
Chapter 4

Numerical Results

4.1 Minimization of the Responsive Oil Model

The minimization of the grand potential with respect to droplet radius \(a\) is implemented numerically, with the system parameters of table 4.1. For different values of droplet radius \(a\), the Poisson-Boltzmann equation with the following boundary conditions is solved numerically

\[
\frac{d^2 \phi(r)}{dr^2} + \frac{2}{r} \frac{d\phi(r)}{dr} = \kappa^2 a^2 \sinh \phi(r),
\]

\[
\phi'(\infty) = 0 \quad \text{and} \quad \phi'(a) = -4\pi \lambda_B a \sigma = -\frac{\lambda_B}{a}(Z_c - Z_a),
\]

where \(\phi(r)\) is the dimensionless potential and \(\kappa^{-1} = 1/\sqrt{8\pi \lambda_B \rho_s}\) is the Debye length. Assuming the salt concentration of table 4.1, the screening length is \(\kappa^{-1} = 13.6\, \text{nm}\). After the electrostatic potential is found numerically, the grand potential can be calculated for several radius values. Therefore, the total grand potential per unit volume can be plotted as a function of the droplet radius, and the radius that minimizes this quantity is the thermodynamically stable state.

Table 4.1: Parameters

<table>
<thead>
<tr>
<th></th>
<th>(\lambda_B)</th>
<th>0.71 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bjerrum length</td>
<td>(\lambda_B)</td>
<td>0.71 nm</td>
</tr>
<tr>
<td>oil-water interfacial tension</td>
<td>(\gamma_{\text{ow}})</td>
<td>8.2 mN/m</td>
</tr>
<tr>
<td>oil volume fraction</td>
<td>(x)</td>
<td>0.002</td>
</tr>
<tr>
<td>ion concentration</td>
<td>(\rho_s)</td>
<td>0.5 mM</td>
</tr>
<tr>
<td>eq. constant oil-cation</td>
<td>(K_c)</td>
<td>(10^{-3}) M</td>
</tr>
<tr>
<td>eq. constant oil-anion</td>
<td>(K_a)</td>
<td>30</td>
</tr>
</tbody>
</table>

In general, the range of the equilibrium constant for cation adsorption and the anion reaction is \(10^{-4} < K_c < 1\, \text{M}\) and \(10^{-5} < K_a < 10^5\) respectively.

The plot of the grand potential as a function of the droplet radius \(a\) is presented at Fig. 4.1(a) and the charge densities of the droplet at Fig. 4.1(b), for the parameters of the table (4.1). The optimal size for a spherical droplet is at radius \(a^* = 11\, \text{nm}\), as seen from the minimum of the red solid line at Fig. 4.1(a). The dashed black line indicates the value of the macroscopic limit, hence the red line is expected to approach monotonically the macroscopic...
The dimensionless grand potential per unit volume is plotted versus the droplet radius $a$. It exhibits a minimum for finite droplet radius, $a = 11\text{nm}$, hence the emulsion is formed spontaneously by oil droplets of such size dispersed inside the water. The dashed line indicates the macroscopic limit.

(b) The absolute value of the charge densities grow in the similar way as the droplet grows. The purple dashed line shows that total charge density at the droplet surface is zero.

Figure 4.1: Grand potential and charge densities plotted as function of the droplet size. The plots correspond to the parameters of table 4.1.

The grand potential is plotted as a function of the droplet size for different oil volume fractions. The optimum droplet radius $a^*$ increases linearly with the addition of oil, as shown by the inset.

(b) The grand potential is plotted with respect to the droplet size for different salt concentrations. The optimal droplet radius $a^*$ decreases with the addition of salt, as shown by the inset.

Figure 4.2: The grand potential is plotted as a function of the droplet size, using the parameters of table 4.1, for different oil volume fractions $x$ and salt concentrations $\rho_s$. 
limit. Fig. 4.1(b) shows that $|\sigma_a|$ and $|\sigma_c|$ charge densities grow in a similar way, such that $\sigma_c + \sigma_a \approx 0$.

Next, we tune composition parameters such as oil volume fraction $x$ and the salt density $\rho_s$, while we keep fixed the other parameters of table 4.1. The resulting plots for $\Omega(a)$ are shown at Fig. 4.2(a) and 4.2(b) respectively. For larger oil volume fractions, the minimum of the potential is moved to bigger radius values, therefore less and larger oil droplets are favorable for the system. In the inset of Fig. 4.2(a), it is shown that the droplet radius increases linearly with the increment of oil volume fraction. On the contrary, for larger salt concentrations, the state of more and smaller droplets is optimal. In the inset of Fig. 4.2(b), the droplet radius is shown to decreases with the addition of salt. The value of the grand potential at the minimum radius also decreases with the addition of salt, while the macroscopic limit, indicated by the thin horizontal black dashed line, does not change. Hence, the addition of salt results to more stable systems with smaller and more droplets.

![Diagram](image)

(a) Both reactions (3.2) and (3.3) are assumed. The reaction terms (purple and blue dashed lines) compete with the interfacial term (black dashed line), giving a finite minimum for the total grand potential (green solid line).

(b) Considering only reaction (3.2), the interfacial term (black dashed line) dominates. The effect of this reaction (blue line) is not enough to compensate the interface term.

Figure 4.3: The contributions to the grand potential are plotted as function of the droplet size, considering both reactions and only the reaction (3.2), using the parameters of table 4.1. The contributing terms are plotted with dashed lines and the total grand potential by solid green line. The black dashed line is the interface term. The red dashed line is the contribution of the ionic electrostatic interaction. The blue dashed line is the adsorption term of reaction (3.2), as given by Eq. (3.6) and the purple dashed line is the contribution of the reaction (3.3), as given by Eq. (3.8).
4.2 Considering Only One Reaction

The hypothetical case, that only one of the reactions (3.2) and (3.3) takes place, is also studied numerically by assuming that the equilibrium constant of one of the reactions goes to infinity.

As we noticed from several numerical attempts for different parameters, the cation adsorption (3.2) exhibits a minimum at the macroscopic limit $a \to \infty$, as shown in Fig. 4.3(b). Considering only the anion reaction (3.3), it is possible to find sets of parameters, that give minima at finite radius, however the minima are less deep than the case that both reactions occur. The grand potentials of the two reactions differ only by the term of the free methanol, apparently it is an important term towards the minimization at a finite radius. Assuming both or one reaction changes the boundary conditions of the PB equation, therefore the resulting electrostatic potential.

The contributions of each term of the grand potential (3.5) are presented in Fig. 4.3. In the case that only reaction (3.2) occurs, the leading term is the interface term. The interface term is the black dashed line at both Fig. 4.3(a) and 4.3(b), it decays as $1/a$. The red dashed line is the contribution of the electrostatic interaction among the ions. The blue dashed line is the adsorption term of reaction (3.2), as given by Eq. (3.6). At Fig. 4.3(a), the purple dashed line is the contribution of the reaction (3.3), as given by Eq. (3.8). At Fig. 4.3(b), where we assume only one reaction, the purple line is zero and the total grand potential, given by the green solid line, goes monotonically to the macroscopic limit. However, in the case of both reactions Fig. 4.3(a), the reactions contributions to the grand potential compensate the interfacial term.

4.3 Buffering Methanol

The case of background methanol density 3.2.3, is also solved numerically. Tuning the background methanol the equilibrium of the chemical reactions is shifted and the entropic contribution of the methanol molecules in the grand potential $\Omega_2$ changes, see Eq. (3.20).

The resulting grand potential $\Omega(a)$ is presented at Fig. 4.4, using the parameters of table 4.1 for several background methanol densities. Increasing the background methanol density, the minima are deeper and shifted to smaller droplet radius, as also shown by the insets of the Fig. 4.4.

At Fig. 4.4(b), the contributing terms to the total grand potential are plotted with dashed lines for background methanol $\rho_m = 0.4mM$. The black dashed line is the interface term. The red dashed line is the contribution of the ionic electrostatic interaction. The blue dashed line is the adsorption term of reaction (3.2), as given by Eq. (3.6) and the purple dashed line is the contribution of the reaction (3.3), as given by Eq. (3.8). The total grand potential is shown by the solid green line. Comparing with Fig. 4.3(a), where the background methanol density is zero, we notice that the addition of methanol influences the contribution of both reaction terms given by Eq. (3.6) and Eq. (3.8).
(a) Plot of the grand potential versus the droplet radius for several background methanol densities $\rho_m$. The insets show the radius that minimizes the grand potential $a^*$ and the difference $\Delta \Omega$ of the minimum value of the grand potential $\Omega^*$ from the macroscopic limit versus $\rho_m$, respectively. The addition of background methanol density results to smaller and more stable droplets.

(b) For $\rho_m = 0.4\text{mM}$, each contributing terms of the grand potential is plotted. Each line represents the same as in Fig. (4.3). Comparing with Fig. (4.3(a)), we notice that the addition of methanol influences the contribution of both reaction terms.

Figure 4.4: The grand potential is plotted with respect to the droplet radius, using the parameters of table (4.1), for several background methanol densities $\rho_m$.

### 4.4 Comparing with Recent Experiments

Recently, there have been several experiments about the formation and the stability of Pickering emulsions [4, 2]. The experimental findings suggest a new class of thermodynamically stable meso-emulsions, as indicated by the spontaneous formation and the monodisperse droplet size, which depends on the system parameters.

For a long time, Pickering emulsions have been considered to be thermodynamically unstable. They required supplied energy to compensate the surface energy upon droplet splitting, hence cannot form spontaneously. They can only be kinetically stable, because the oil and water phases separate again in the long run. However, the new experimental findings of a specific type of Pickering emulsion [4, 2], consisting of a particular oil TPM (3-(Methacryloxypropyl)tri-methoxysilane), an aqueous solution of TMAH salt (Tetramethylammonium hydroxide) and magnetite particles of size 11nm, show that the emulsion forms spontaneously, without shaking or ultrasonication. The thermodynamic stability is proven by mixing two emulsions of different droplet sizes that spontaneously evolved into an emulsion of intermediate droplet size. Moreover, the thermodynamic stability is indicated by the monodisperse size of the droplets, which is determined by the mass ratio of TPM and magnetite colloidal particles.

In this section, we present the results of our theoretical model and compare them with
According to [2], the description of the chemical processes that take place is summarized at the experimental findings of section IV.1 of [2], about emulsions without colloidal particles. Data.

The chemical reactions are characterized by the equilibrium constants. From the bibliography or a hydrocarbon group. They belong to the wider class of organosilicon compounds.

Alkaline conditions characterized by excess of hydroxide OH\(^{-}\), hence pH > 7.

Silanols are compounds containing silicon atoms to which hydroxyl –OH substituents bond directly.

A siloxane is any chemical compound composed of units of the form \( R_2 SiO \), where \( R \) is a hydrogen atom or a hydrocarbon group. They belong to the wider class of organosilicon compounds.

---

Figure 4.5: Experimental picture of Pickering emulsions without colloidal particles and auxiliary plot of the unknown equilibrium constants \( \{K_c, K_a\} \) in order to fit the experimental data.

The experimental findings of section IV.1 of [2], about emulsions without colloidal particles. According to [2], the description of the chemical processes that take place is summarized at the following points:

- The TMAH salt shifts the pH towards alkaline conditions \(^1\) hence enhance the hydrolysis of TPM oil and probably also acts as a catalyst in the reaction. However, it also speeds up the self-condensation reaction of the formed silanols \(^2\) into siloxane \(^3\) linkages [12].

- Hydrolyzed TPM molecules can dissociate forming negatively charged surface active molecules, which can be adsorbed by the oil water interface, therefore lower the interfacial tension.

The chemical reactions are characterized by the equilibrium constants. From the bibliography

---

\(^1\)Alkaline conditions characterized by excess of hydroxide OH\(^{-}\), hence pH > 7.

\(^2\)Silanols are compounds containing silicon atoms to which hydroxyl –OH substituents bond directly.

\(^3\)A siloxane is any chemical compound composed of units of the form \( R_2 SiO \), where \( R \) is a hydrogen atom or a hydrocarbon group. They belong to the wider class of organosilicon compounds.
The equilibrium constant for the esterification of silanols is given

\[ K_{eq} = \frac{[R_3SiOCH_3][H_2O]}{[R_3SiOH][CH_3OH]} = 2.5 \cdot 10^{-2}. \]  

(4.2)

This value is a good estimate for the hydrolysis of TPM. However, to match with the equilibrium constant of the reaction (3.3), it should be multiplied with the equilibrium constant of the dissociation of the hydrolyzed TPM oil and the equilibrium constant of the adsorption of the negatively charged molecules at the water oil interface.

Table 4.2: Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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</thead>
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<tr>
<td>Bjerrum length</td>
<td>( \lambda_B ) 0.71 nm</td>
</tr>
<tr>
<td>Oil-water interfacial tension</td>
<td>( \gamma_{ow} ) 8.2 mN/m</td>
</tr>
<tr>
<td>Ion concentration</td>
<td>( \rho_s ) 6 mM</td>
</tr>
<tr>
<td>Oil volume fraction</td>
<td>( x ) 0.01</td>
</tr>
</tbody>
</table>

![Graph](image)

(a) The experimentally measured droplet radius with the experimental error are shown by black stars, for four different values of oil volume fraction. The two lines are obtained by the numerical data of our theoretical model for two different pairs of equilibrium constants. The radius of the droplets scales linearly with the TPM oil volume fraction.

(b) Several curves of the grand potential versus the droplet radius \( a \), corresponding to oil volume fractions \( x \) of the experimental data. The equilibrium constants used are \( K_c = 0.4M \) and \( K_a = 40 \). The droplet size grows with the addition of oil and the observed minima become less deep. For example, at \( x = 0.02 \) the macroscopic limit of the grand potential is \(-1.98 \) and the finite minimum occur at \(-1.99 \).

Figure 4.6: Fitting to the experimental data [2] and the minimization of the grand potential for system parameters of table (4.2).

---

[4]Esterification is the general name for a chemical reaction in which two reactants (typically an alcohol and an acid) form an ester as the reaction product.
For the values of the two last equilibrium constants, no estimates can be found in the literature. For this reason, the equilibrium constants, $K_c$ and $K_a$, are to be considered as free parameter within the above mentioned range, section 4.1. To choose the equilibrium constants for the two reactions, (3.2) and (3.3), random pairs of values are tested for the system parameters of table 4.2.

The pairs $\{K_c, K_a\}$ for which the resulting minimization radius is close to the measured one, are shown in Fig. 4.5(b). The black dots are pairs of values for $\{K_c, K_a\}$ which result to minimization radius within the experimental error. The red stars correspond to pairs which result to the measured experimental value. The experimental measurements of the droplet sizes for different oil volume fractions are shown in Fig. 4.6(a) (black stars with error bars).

The experimental data are obtained by the preparation of samples containing 6mM of TMAH and different volume fractions of TPM oil, within the range $x \in [0.005, 0.025]$. A day after the preparation, by gentle mixing, the samples turned turbid and the turbidity increased by the oil volume fraction. After several days, the emulsions become unstable and finally phase separate. The experimental results are presented at Fig. 4.5(a). During the stable period of the prepared emulsions, the droplet size was measured. The experimental data are shown at Fig. 4.6(a) by black stars with the experimental error. The two lines, shown at Fig. 4.6(a), are obtain by the numerical data of our theoretical model for two different pairs of equilibrium constants. The first pair, represented by the red solid line, was chosen to fit the data point of $x = 0.01$. The second pair, which results at the purple dashed line, was chosen within the error of the data point of $x = 0.01$. The experimental and numerical result of this plot is that the radius of the droplets scales linearly with the TPM oil volume fraction. In Fig. 4.6(b), the grand potential with respect to the droplet radius is plotted for several oil volume fraction, in the range of the experimental data. The droplet size and minimum value of the grand potential increases with the oil volume fraction, resulting to less stable systems.

Considering the equilibrium constants $\{K_c, K_a\} = \{0.4M, 40\}$, the dependence of the droplet size by the oil volume fraction $x$ and the salt density $\rho_s$ is presented by the density plots of Fig. 4.7(a). The areas of lighter color depict pairs of $\{x, \rho_s\}$ that result to smaller oil droplets, while the darker areas correspond to larger droplets.

The two important aspects of Pickering meso-emulsions are the spontaneous formation and the thermodynamic stability. The theoretical model describes the spontaneous formation for a broad range of system parameters, where the grand potential is minimized at a finite radius. The experiments confirm the spontaneous formation of emulsion even though colloidal particles are absent. However, emulsions without colloidal particles are not thermodynamically stable in the experiments. The chemical effect that results to the destabilization of the emulsion is probably the self-condensation reaction of silanols into siloxane linkages. The self-condensation reaction is much slower than the TPM hydrolysis, hence it plays a role at a larger time scale. This reaction is absent from our theoretical model, therefore the ultimeta phase separation of the system cannot be captured.

A way to effectively include the self condensation reaction is by varying with time the equilibrium constant $K_a$ of reaction (3.3). As shown at Fig. (4.7(b)), the droplets become bigger increasing the equilibrium constant $K_a$ and the minimum value of the grand potential goes to the macroscopic limit. By assuming that the equilibrium constant $K_a$ incorporates the self condensation reaction and increases by time, we can see the different droplet sizes in the passing of time. Unfortunately, the time behavior of intrinsic parameters of the system,
4.5 Conclusions

The spontaneous formation of an emulsion is a collective effect, it depends on the balance of the contributing effects. The presence and the intensity of each one of the contributing interactions can affect the formation and the characteristics of an emulsion, such as the droplet size and the stability. Including the electrostatic interactions among the ions and between the ions and the charged droplets, the adsorption of ions into the oil-water interface and the surface tension of the oil droplets, the formation of a thermodynamically oil-water emulsion is possible within a reasonable range of system parameters.

The favorable state of oil and water would be to not mix in the absence of energy input, thus the surface term would be the leading term. In case of this type of emulsions, the chemical reactions, therefore the electrostatic interactions and the adsorption, offer the required free energy to form an emulsion spontaneously. In terms of the grand potential (3.5), the electrostatic term and the adsorption terms compensate the surface tension term, resulting to an equilibrium system, consisting of oil droplets of tens of nanometers, a meso-emulsion.

In our theoretical model, we included two reactions to represent the chemical processes observed in the experiments. If the hydrolysis reaction (3.3) is absent, the emulsion is not formed spontaneously. If the reaction (3.2) is absent, the emulsion is formed, however the
resulting minimum is less deep than the case of both reactions. Therefore, the adsorption effects determine the spontaneous formation of emulsions and their stability.

Tuning the parameters of the theoretical model the characteristics of the emulsions change. First, we tune the composition parameters, such as the oil volume fraction $x$ and the salt concentration $\rho_s$. Increasing the oil volume fraction $x$, the forming oil droplet are bigger and the equilibrium grand potential does not change significantly. In comparison, increasing the salt concentration $\rho_s$, the oil droplets are smaller and the minimum of grand potential becomes smaller. Secondly, we add methanol with background concentration $\rho_m$, which results to smaller droplets and smaller grand potential. An interesting remark is that the equilibrium droplet radius does not change significantly, however the difference of the grand potential from the macroscopic limit at the equilibrium radius decreases significantly, suggesting a stabler system.

We also tune the intrinsic parameters of the system, such as the equilibrium constants $K_c, K_a$ of the two reactions. Actually the equilibrium constants are considered to be free parameters, as there is not sufficient value in the bibliography. It is also possible that the equilibrium constants change through time, as new phenomena take place, such as the self condensation reaction. Hence, we tested a broad range of values for the two equilibrium constants, finding that several pairs of \{K_c, K_a\} result to the same size of oil droplets. Tuning the equilibrium constants for a given oil and salt composition of the system, we find that the system can form larger droplets. According to experimental findings, some time after the formation of the emulsion, the droplets coalesce and finally the系统 phase separates. Assuming that time dependent equilibrium constants could capture the reaction effects through time, then the kinetically stable states that the system reaches through time, can be described by this theoretical model.
Bibliography


Appendix A

Theoretical and Numerical Supplement

A.1 Dimensionless Form of PB Equation

The dimensionless form of equation reduces the number of parameters and it is easier and safer to apply approximations by considering a quantity small. The dimensional analysis is applied on the Poisson-Boltzmann equation,

\[ \nabla^2 \phi(r) = \kappa^2 \sinh \phi(r) \tag{A.1} \]

in spherical coordinates, assuming that the potential \( \phi(\vec{r}) \) is symmetric over the polar \( \theta \) and the azimuthal \( \phi \) angle,

\[ \frac{d^2 \phi(r)}{dr^2} + \frac{2}{r} \frac{d \phi(r)}{dr} = \kappa^2 \sinh \phi(r). \tag{A.2} \]

Consider the dimensionless length \( x = r/\gamma \), where \( \gamma \) is a characteristic length scale. The characteristic length is such that the derivatives in the new coordinates are of unity order \( \mathcal{O}(1) \). The new derivatives are expressed using the chain rule

\[ \frac{d \phi(r)}{dr} = \frac{d \phi(x)}{dx} \frac{dx}{dr} = \frac{1}{\gamma} \frac{d \phi(x)}{dx} \tag{A.3} \]

and similarly

\[ \frac{d^2 \phi(r)}{dr^2} = \frac{1}{\gamma^2} \frac{d^2 \phi(x)}{dx^2}. \tag{A.4} \]

Applying the above substitutions to PB equation (A.2) results to

\[ \frac{1}{\gamma^2} \frac{d^2 \phi(x)}{dx^2} + \frac{2}{r \gamma} \frac{d \phi(x)}{dx} = \kappa^2 \sinh \phi(x). \tag{A.5} \]

The dimension of the PB equation (A.1) is \([m^{-2}]\), as can easily be seen from the right hand side of the equation (A.2), as the Debye length \( \kappa \) has dimension of inverse length. In order to obtain a dimensionless equation, it should multiplied by a squared length. As characteristic
length, the radius $a$ of the charged sphere or the Bjerrum length $\lambda_B$ are possible candidates. Here we chose the sphere radius $a$, therefore

$$\frac{a^2}{\gamma^2} \frac{d^2\phi(x)}{dx^2} + \frac{2a^2}{r} \frac{d\phi(x)}{dx} = \kappa^2 a^2 \sinh \phi(x).$$  \hspace{1cm} (A.6)$$

Since $\sinh \phi$ and the derivatives are of order $O(1)$ by assumption, then

$$\frac{a^2}{\gamma^2} \approx O(1) \quad \text{such that} \quad \gamma = a. \hspace{1cm} (A.7)$$

The dimensionless form of PB equation follows

$$\frac{d^2\phi(x)}{dx^2} + \frac{2}{x} \frac{d\phi(x)}{dx} = \kappa^2 a^2 \sinh \phi(x).$$  \hspace{1cm} (A.8)$$

The boundary conditions in case of a charged sphere of radius $a$ are

$$\left. \frac{d\phi(r)}{dr} \right|_{r \to \infty} = 0 \quad \text{and} \quad \left. \frac{d\phi(r)}{dr} \right|_{r = a} = -4\pi \lambda_B \sigma, \hspace{1cm} (A.9)$$

where $\lambda_B$ is the Bjerrum length, $\sigma = Z/(4\pi a^2)$ the surface charge. The dimensionless boundary conditions are

$$\left. \frac{d\phi(x)}{dx} \right|_{x = \infty} = 0 \quad \text{and} \quad \left. \frac{d\phi(x)}{dx} \right|_{x = 1} = -4\pi \lambda_B a \sigma = -\frac{\lambda_B}{a} Z. \hspace{1cm} (A.10)$$

A.2 Euler method

A numerical solution to the nonlinear PB equation can be acquired by Euler’s method. This scheme provides a way to approximate the solution $\phi(r)$ given the equation and satisfactory number of initial conditions.

According to Euler’s method, starting from the initial condition of the function, we can find the next point by moving in the direction of the derivative, so the iteration scheme follows

$$f(x_{n+1}) = f(x_n) + f'(x_n) \Delta x$$  \hspace{1cm} (A.11)$$

where $\Delta x$ should be very small, otherwise the approximation gets bad.

We will apply the iterative method to PB equation (A.2). Firstly, we consider a grid for the distance $r$, $r(n+1) = r(n) + \Delta r$, where $\Delta r$ is given by the total number of iteration points $N$, $\Delta r = R/N$ with $R$ the total interval of interest. Then, we set $u(r)$ the first derivative of the potential $u(r) = \phi'(r)$, where by one prime we mean the first derivative with respect to $r$ and by two primes the second derivative. Therefore, the PB equation is written

$$u'(r) = -\frac{2}{r} u(r) + \sinh \phi(r)$$  \hspace{1cm} (A.12)$$

To approximate the value of the potential for the next grid point, the derivative at the previous point should be known, which involves also the value of the potential at the previous point.
as can be seen by equation (A.12), then the two functions $u(r)$, $\phi(r)$ are interconnected. The system of equations is

$$u(r_{n+1}) = u(r_n) + u'(r_n) \Delta r$$
$$\phi(r_{n+1}) = \phi(r_n) + u(r_n) \Delta r$$

(A.13)

if we impose two initial conditions, for the potential and its derivative, the above system can be solved numerically.

### A.3 Definitions of Physical quantities

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_B$</td>
<td>Bjerrum length</td>
<td>$\lambda_B = \frac{e^2}{\epsilon \kappa_B T}$</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>Debye length</td>
<td>$\kappa^{-1} = \sqrt{8 \pi \lambda_B \rho}$</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>interfacial tension</td>
<td>$\gamma = \frac{dW}{dA}$</td>
</tr>
<tr>
<td>$e$</td>
<td>elementary charge</td>
<td></td>
</tr>
<tr>
<td>$\beta$</td>
<td>inverse thermal energy</td>
<td>$\beta = \frac{1}{k_B T}$</td>
</tr>
<tr>
<td>$\Lambda$</td>
<td>thermal de Broglie length</td>
<td>$\Lambda = \frac{\hbar}{\sqrt{2 \pi \hbar k_B T}}$</td>
</tr>
<tr>
<td>$K$</td>
<td>equilibrium constant</td>
<td>$K = \frac{</td>
</tr>
</tbody>
</table>